Molecular and supramolecular C_{60}–oligophenylenevinylene conjugates

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Fullerene derivatives are attractive building blocks for the preparation of molecular and supramolecular photoactive devices. As a part of this research, combination of C_{60} with oligophenylenevinylene (OPV) subunits has generated significant research efforts. These results are summarized in the present account to illustrate the current state-of-the-art of fullerene chemistry for the development of new photoactive materials.

Introduction

In recent years, the rapid advances in fullerene synthetic chemistry[1] have moved towards the creation of functional systems with increased attention to potential applications.[2] In particular, the unique electronic properties of C_{60} have generated significant research activities focused on its use as an electron and/or energy acceptor in photochemical molecular devices.[3] The combination of the carbon sphere with π-conjugated oligomers for the construction of donor–fullerene arrays is of particular interest. On one hand, such hybrid systems have shown excited state interactions making them excellent candidates for fundamental photophysical studies. On the other hand, covalently linked fullerene–π-conjugated oligomer derivatives have been used as the active layer in organic photovoltaic cells.[4] This approach using molecular dyads as the active layer in solar cells is particularly interesting since it restricts the dimension of the bicontinuous donor–acceptor network on the finest molecular level. The nanoscopic dimension of the phase separation is an advantage because the exciton diffusion length in conjugated systems is limited to that length scale.[4] Another major advantage of this approach is that the behavior of a unique molecule in a photovoltaic cell allows to obtain easily structure–activity relationships for a better understanding of the photovoltaic system.[4] This specific aspect of covalently linked fullerene–π-conjugated oligomer systems has been summarized in several recent review articles[4] and will not be discussed in the present account in which the most recent developments on the molecular engineering of covalent and non-covalent fullerene–oligophenylenevinylene (OPV) conjugates will be presented. The aim of this article is not to show an exhaustive review on C_{60}–π-conjugated oligomer systems but to present significant examples to illustrate the current state-of-the-art of fullerene chemistry for the development of new photoactive materials. For this reason, only hybrid systems combining C_{60} and OPV moieties will be considered.

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Covalent fullerene–OPV photoactive devices

Compounds **1–3** are the first examples of reported covalent fullerene–OPV dyads (Fig. 1).[5–7] The synthetic approach to prepare **1–3** relies upon the 1,3-dipolar cycloaddition of azomethine ylides generated *in situ* from the corresponding aldehydes and *N*-methylglycine.

Their photophysical properties have been investigated in different solvents (toluene, CH_2Cl_2 and benzonitrile). Upon selective excitation of **1–3** on the fullerene fragment, the typical fulleropyrrolidine fluorescence and triplet–triplet transient absorption spectra are observed.[6,7] This indicates that the excited state properties of the C_{60} fragment are not affected by the presence of the nearby OPV moieties. On the other hand, when excitation is addressed to the latter, intercomponent

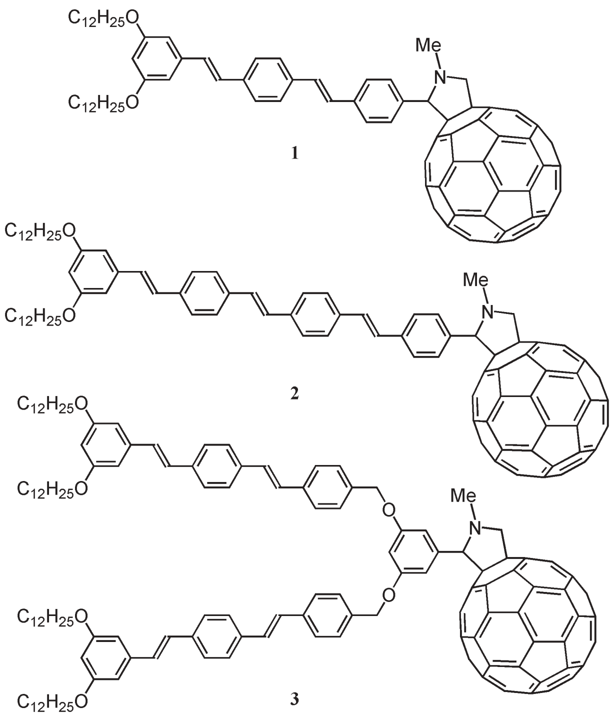


Fig. 1 C_{60}–OPV conjugates **1–3**.

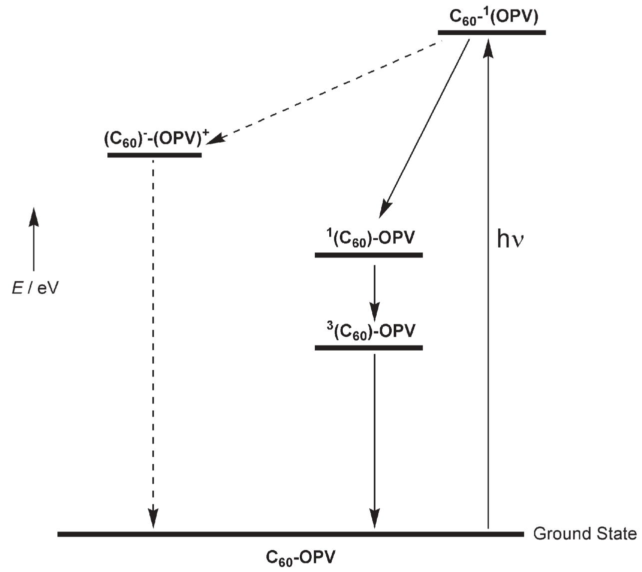
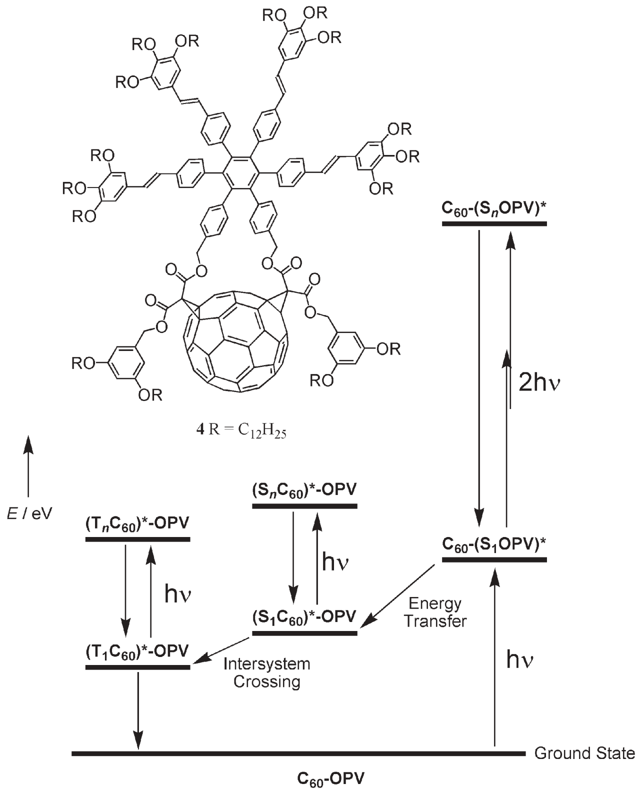


Fig. 2 Energy-level diagram describing the excited-state deactivation pathways and the intercomponent processes for the C_{60}–OPV hybrid compounds **1–3**.

processes are evidenced. Under such conditions, the intense fluorescence band characteristic of the OPV moiety is not observed, whereas the typical fluorescence band of the fulleropyrrolidine fragment is detected at *ca.* 710 nm. In addition, the fullerene fluorescence quantum yields of **1–3** are identical to that of a model fulleropyrrolidine derivative, although at least 85% of the incident light is absorbed by the OPV fragments. The excitation spectra of **1–3**, taken at λ_{em} = 710 nm, well matches the absorption profile throughout the UV/Vis, including the diagnostic band of the OPV moieties. These findings are consistent with quantitative occurrence of singlet–singlet energy transfer from the OPV unit to the fullerene in the multicomponent arrays **1–3**. From the electrochemical data one can place the energy of the charge separated state of **1–3** at about 1.9–2.0 eV, *e.g* well below the energy of the lowest singlet excited state of the OPV moieties (2.9–3.1 eV) (Fig. 2). However, even if the population of the charge separated state following photoexcitation of the OPV unit is thermodynamically allowed, this process is not evidenced in CH_2Cl_2 solution. The use of polar solvents does not change the observed pattern; for instance, an evidence for quantitative OPV → C_{60} singlet–singlet energy transfer is also observed in benzonitrile solution. Model calculations on the OPV → C_{60} singlet–singlet energy transfer step by following the dipole–dipole (Förster) approach result in an estimated rate constant, $k_{en} \gg 10^{12}\ s^{-1}$.[6,7] This estimate suggests that the energy transfer step is so fast that the competing charge separation path is not effective. The nearly quantitative singlet-singlet OPV → C_{60} photoinduced energy transfer was an important finding as it explained the low efficiencies of the photovoltaic devices prepared from compounds **1–3**. Indeed, the main part of the light energy absorbed by the OPV moiety is conveyed to the fullerene by energy transfer and, since electron transfer from the fullerene lowest singlet excited state is not possible due to its low energy content, electron–hole pairs cannot be generated any more. Thus, only a small part of the absorbed light is able to contribute effectively to the photocurrent.[5,6]

Recently, the synthesis and the excited state properties of compound **4** assembling C_{60} with a branched OPV-based chromophore have been reported (Fig. 3).[8] As already seen for compounds **1–3**, nearly quantitative singlet–singlet OPV → C_{60} photoinduced energy transfer occurs in compound **4**. However, the excited state dynamics of **4** have been found more complicated as the branched OPV-based system is a multi-photon absorption (MPA) chromophore. Thus, hybrid compound **4** combines two different optical limiters, the fullerene which is a reverse saturable absorption system[9] and the branched OPV unit which is an excited-state MPA chromophore.[10] Specifically, in the latter case, a first one-photon transition populates an excited state of the molecule, then a two-photon absorption from this excited state occurs.[8] Interestingly, compound **4** shows enhanced optical limiting properties when compared to a 1 : 1 mixture of the separate components. When the two moieties are covalently linked, deactivation of the lowest singlet excited state of the conjugated system C_{60}–$(S_1OPV)^*$ occurs by quantitative OPV → C_{60} singlet–singlet energy transfer, thus populating the lowest fullerene singlet excited state $(S_1C_{60})^*$–OPV. As the latter possesses a larger cross-section than the ground state, it is itself also involved in the non-linear behaviour. For this reason, the combination of a MPA chromophore with C_{60} leads to improved optical limiting properties. These findings pave the way towards the design of new efficient fullerene-based singlet oxygen sensitizer for photodynamic therapy applications. Effectively, hybrid systems combining C_{60} and conjugated oligomers with strong MPA should be capable of generating singlet oxygen upon multi-photon absorption[11]



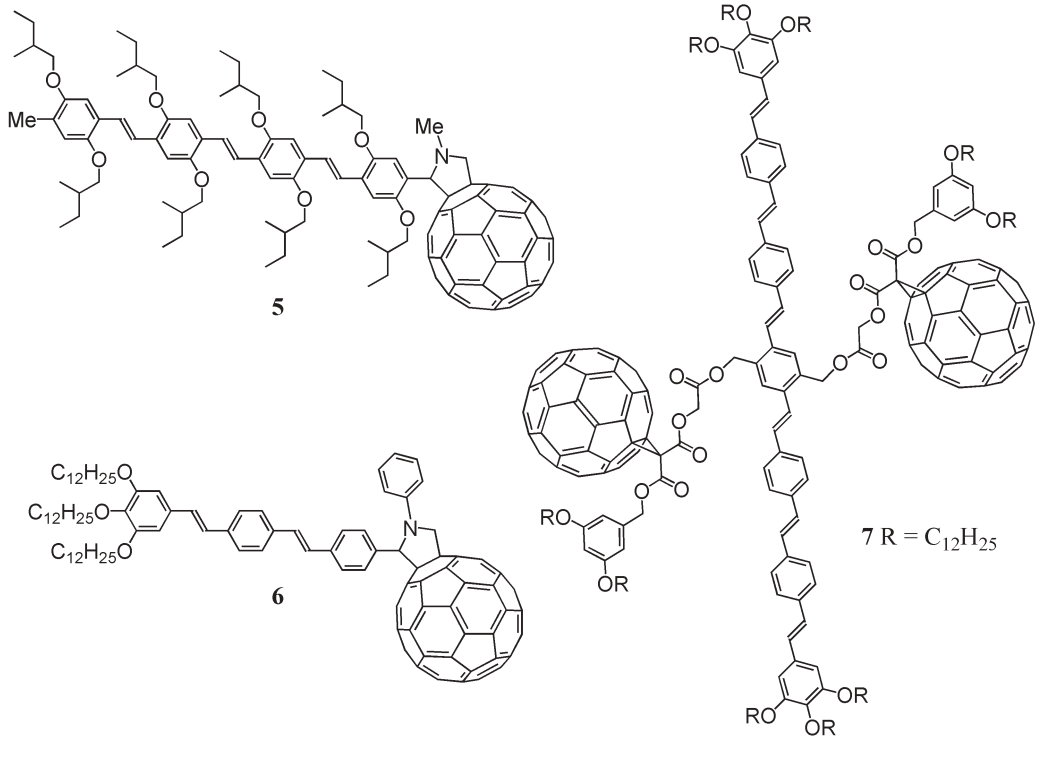
4 R = $C_{12}H_{25}$

Fig. 3 Energy-level diagram describing the optical limiting properties of the C_{60}–OPV hybrid compound **4**.

followed by energy transfer to the fullerene sensitizing unit.[12] This could broaden the applicability of C_{60} derivatives in photodynamic therapy[13] which is currently highly limited by both the weak linear and the low induced absorptions of fullerene-based sensitizers in the 650–750 nm region. For such an application, the combination of C_{60} with an appropriate ground state MPA dye will be necessary.

The C_{60}–OPV hybrid compound **5** has been reported by Hummelen, Janssen and coworkers (Fig. 4).[14] The photophysical properties of **5** have been systematically investigated in solution with solvents of different polarity. Photo-excitation of the OPV moiety in a non-polar solvent (toluene) led to an ultrafast singlet energy transfer from the OPV toward the C_{60} subunit. This ultrafast energy transfer is followed by a nearly quantitative inter-system crossing to the C_{60} triplet state.

On the other hand, in a more polar solvent (*o*-dichlorobenzene), photo-excitation of the OPV moiety resulted in electron transfer from the OPV to the C_{60} subunit with formation of a charge-separated state. To rationalize the observed differences in apolar and polar solvents, the changes in free energy for charge separation of this donor–acceptor system have been calculated from the Weller equation. It appeared that in toluene, the charge-separated state is higher in energy than the first fullerene singlet and triplet excited states (Fig. 5). Therefore, the light energy absorbed by the OPV fragment promptly conveyed to the fullerene lowest singlet excited state *via* energy transfer cannot yield charge-separation anymore. In a more polar solvent, the situation is completely different, because the energy of the charge-separated state drops below that of the first fullerene singlet excited state allowing occurrence of electron transfer after the initial singlet energy transfer event (Fig. 5). Similar findings about lowering the energy of the charge-separated state by increasing the solvent polarity, have been also reported by Guldi, Martin and co-workers[15] for a series of



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7 R = $C_{12}H_{25}$

Fig. 4 C_{60}–OPV conjugates **5–7**.

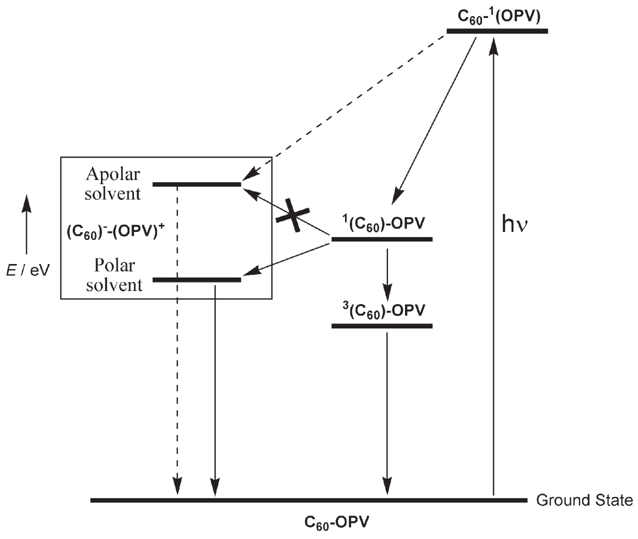
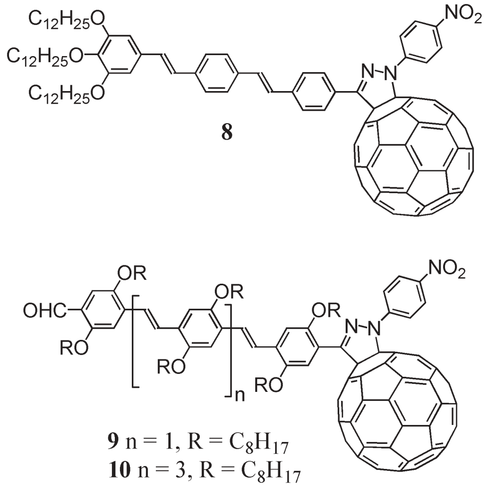


Fig. 5 Energy-level diagram describing the excited-state deactivation pathways and the intercomponent processes in solvents of different polarities for the C_{60}–OPV hybrid compounds **5–7**.

oligo(naphthylenevinylene)–fullerene dyads, and Armaroli *et al.* for fullerene–OPV derivatives **6** and **7** (Fig. 4).[16,17]

Related fullerene derivatives in which an OPV subunit is attached to C_{60} through a pyrazoline ring have also been reported (Fig. 6).[16,18] In this case, the excited-state properties are more complex due to the electron donating ability of the pyrazoline ring. As observed for **5–7**, quantitative OPV → C_{60} photoinduced singlet–singlet energy transfer occurs in **8–10** in CH_2Cl_2. However, the population of the lowest fullerene singlet excited state is followed by an efficient electron transfer from the N lone pair of the pyrazoline ring in **8–10**.

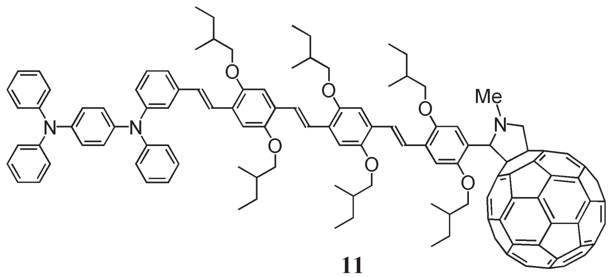
More elaborated systems in which an additional donor subunit has been connected to the C_{60}–OPV system have also been described. An example of such donor-donor–acceptor triads is depicted in Fig. 7. In this case, the additional donor is a *p*-oligoaniline (OAn) moiety.[19] By using a *meta*-substituted phenylene ring in OAn–OPV–C_{60}, the OAn and OPV parts are almost electronically decoupled in the ground state and operate as isolated redox active segments. In **11**, the oxidation potential decreases from C_{60}, *via* OPV, to OAn, while at the same time the reduction potential increases. By introducing this redox gradient, the energetically most favorable charge-separated state corresponds to OAn^+–OPV–C_{60}^-. Detailed analysis of the photophysical processes in **11** has been performed using photoluminescence and femtosecond pump–probe spectroscopy in solvents of different polarity. Photoexcitation of any of the three chromophores of this triad in a polar solvent results in the formation of the OAn–OPV^+–C_{60}^- charge-separated state, after an efficient ultrafast (<190 fs) singlet-energy transfer to the fullerene singlet excited state. The initial OAn–OPV^+–C_{60}^- state can rearrange to the low-energy OAn^+–OPV–C_{60}^- charge separated state *via* an intramolecular redox reaction. Because the competing charge recombination of the OAn–OPV^+–C_{60}^- state to the ground state is fast and increases with increasing polarity of the solvent, the quantum yield for this charge shift is the highest (*ca.* 40%) in weakly polar solvents such as chlorobenzene. Once formed, the OAn^+–OPV–C_{60}^- state has a long lifetime (>1 ns) due to weak electronic coupling between the distant redox sites in the excited state. The stabilization gained is more than one order of magnitude in time.



8

9 n = 1, R = C_8H_{17}
10 n = 3, R = C_8H_{17}

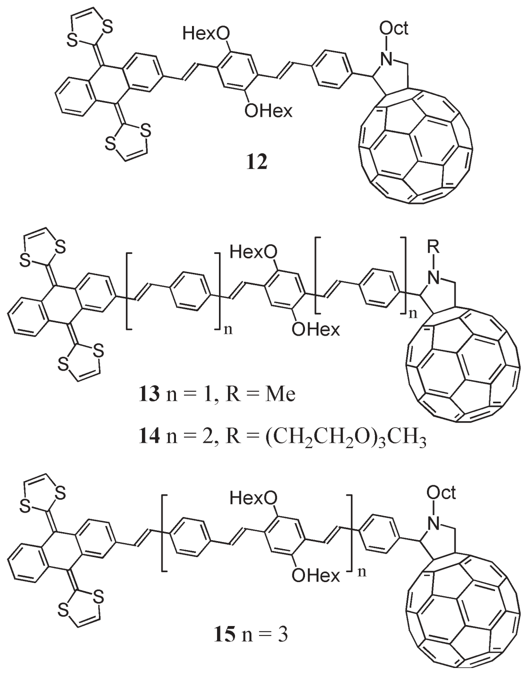
Fig. 6 C_{60}–OPV conjugates **7–9**.



11

Fig. 7 OAn–OPV–C_{60} triad **11**.

Related systems have been reported by Guldi, Martin and co-workers.[20] A series of structurally well-defined arrays (**12–15**) that incorporate a π-extended tetrathiafulvalene (ex-TTF) as electron donor and C_{60} as electron acceptor, linked by OPV moieties of different lengths has been prepared (Fig. 8).[20] In this case, the additional donor (ex-TTF) is conjugated with the oligomeric bridge. The electrochemical studies reveal a lack of significant electronic communication between the donor (ex-TTF) and the acceptor (C_{60}) moieties through the π-conjugated oligomer in **12–15**. However, photoinduced electron transfer leading to the radical pair ex-TTF^+–OPV–C_{60}^- has been evidenced in all these compounds. For **12–14**, the charge-recombination dynamics show the presence of highly stabilized charge-separated states with lifetimes in the range between 465 and 557 ns in benzonitrile, which indicates a very low influence of the oligomer length on the electron rate. These findings clearly indicate a nanowire behaviour. A longer radical-pair lifetime (10 times) has been observed for the heptamer-containing array ex-TTF^+–OPV–C_{60}^-, which has been accounted for by the loss of planarity of the oligomer moiety. The same authors have also studied the electronic communication through OPV wires in related covalently linked porphyrin–OPV–C_{60} ensembles.[21] A similar



12

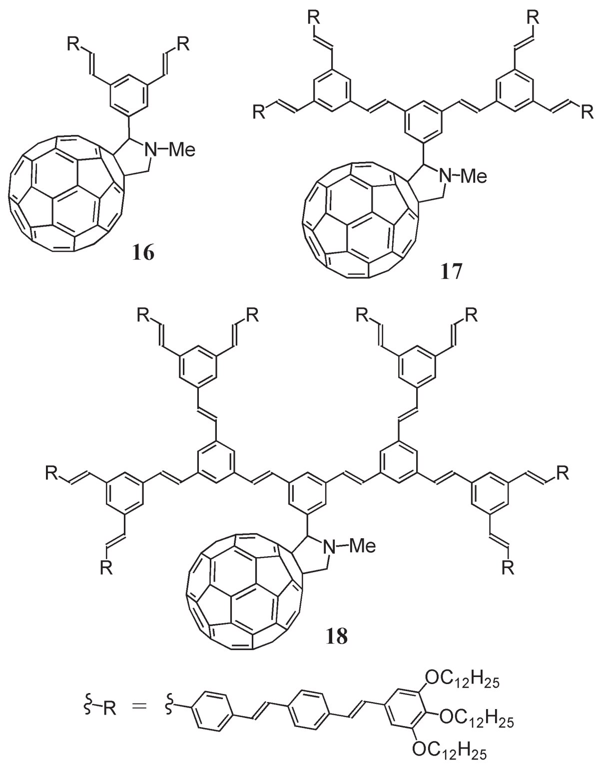
13 n = 1, R = Me

14 n = 2, R = $(CH_2CH_2O)_3CH_3$

15 n = 3

Fig. 8 ex-TTF–OPV–C_{60} triads **12–15**.

wirelike behaviour for the OPV connecting units has been evidenced with this series of compounds.



16

17

18

Fig. 9 Fullerodendrimers with peripheral OPV units.

Dendritic fullerene–OPV systems

Owing to the very efficient singlet–singlet OPV → C_{60} photoinduced energy-transfer, fullerene–OPV conjugates are attractive systems for the preparation of light harvesting dendrimers.[22] In such molecular devices, an array of peripheral chromophores is able to transfer the collected energy to the central core of the dendrimer thus mimicking the natural light-harvesting complex in which antenna molecules collect sunlight and channel the absorbed energy to a single reaction center.[22] With this idea in mind, dendrimers **16–18** with a fullerene core and peripheral OPV subunits (Fig. 9) have been prepared.[23,24]

The photophysical properties of fullerodendrimers **16–18** have been first investigated in CH_2Cl_2 solutions. Upon excitation at the OPV band maximum, dramatic quenching of OPV fluorescence is observed for all fullerodendrimers. At 394 nm (corresponding to OPV band maxima) the molar absorptivities (ε) of these fullerodendrimers are 134 800 for **16**, 255 100 for **17** and 730 400 M^{-1} cm^{-1} for **18**. Since the ε of the ubiquitous *N*-methylfulleropyrrolidine at 394 nm is only 7600 a remarkable light harvesting capability of the peripheral units relative to the central core is evidenced along the series. UV-VIS-NIR luminescence and transient absorption spectroscopy have been used to elucidate in more detail the photoinduced processes in fullerodendrimers **16–18** as a function of the dendritic generation and of the solvent polarity (toluene, CH_2Cl_2, benzonitrile), taking into account that the free energy change for electron transfer is the same along the series due to invariability of the donor–acceptor couple. In any solvents, all of the fullerodendrimers exhibit ultrafast OPV → C_{60} singlet energy transfer (k_{EnT} *ca.* 10^{10}–10^{12} s^{-1}). In CH_2Cl_2, a slightly exergonic OPV → C_{60} electron transfer from the lowest fullerene singlet level ($^1C_{60}$*) is made possible ($\Delta G_{CS} \approx$ 0.07 eV), but it is observed, to an increasing extent, only in the largest systems **17** and **18** characterized by a lower activation barrier for electron transfer. This effect has been related to a decrease of the reorganization energy upon enlargement of the molecular architecture. Structural factors are also at the origin of an unprecedented OPV → C_{60} electron transfer observed for **17** and **18** in non-polar toluene, whereas in benzonitrile electron transfer occurs in all cases.

Related compounds have been reported by Martin, Guldi and co-workers.[25] The end-capping of the dendritic spacer with dibutylaniline units yielded the multicomponent photoactive system **19** in which the dendritic wedge plays at the same time the role of an antenna capable of channeling the absorbed energy to the fullerene core and of an electron donating unit (Fig. 10). Photophysical investigations in benzonitrile solutions have shown that, upon photoexcitation, efficient and fast energy transfer takes place from the initially excited antenna moiety to the fullerene core. This process populates the lowest fullerene singlet excited state which is able to promote electron transfer from the dendritic unit to the fullerene core. Langa and co-workers[26] have prepared fullerodendrimer **20** in which the phenylenevinylene dendritic wedge is terminated with ferrocene subunits. Nanosecond transient absorption spectral studies have shown that efficient charge separation occurs in this system, even in non-polar solvents.

The unusual photophysical properties of C_{60}–OPV hybrid systems have also been used to evidence dendritic encapsulation effects.[27] For this purpose, highly soluble dendritic

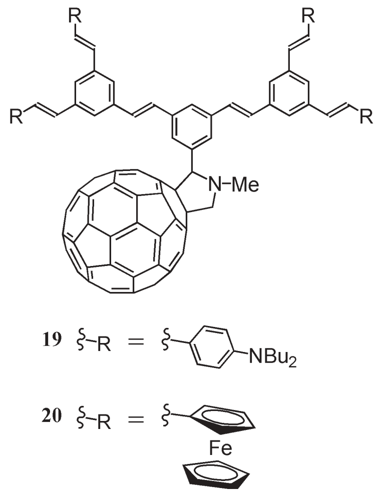


Fig. 10 Fullerodendrimers **19** and **20**.

branches with fullerene subunits at the periphery and a carboxylic acid function at the focal point have been attached to an OPV core bearing two alcohol functions to yield dendrimers **21–23** with two, four or eight peripheral C_{60} groups, respectively (Fig. 11).[28]

The photophysical properties of **21–23** have been systematically investigated in solvents of increasing polarity *i.e.* toluene, dichloromethane, and benzonitrile. Ultrafast OPV → C_{60} singlet energy transfer takes place for the whole series of dendrimers, whatever the solvent is. Electron transfer from the fullerene singlet is thermodynamically allowed in CH_2Cl_2 and benzonitrile, but not in apolar toluene. For a given solvent, the extent of electron transfer, signaled by the quenching of the fullerene fluorescence, is not the same along the series, despite the fact that identical electron transfer partners are present. By increasing the dendrimer size, electron transfer is progressively more difficult. Practically no electron transfer from the fullerene singlet occurs for **23** in CH_2Cl_2, whereas some of it is still detected in the more polar PhCN. These trends can be rationalized by considering increasingly compact dendrimer structures in more polar solvents.[28] This implies that the actual polarity experienced by the involved electron transfer partners, particularly the central OPV, is no longer that of the bulk solvent. This strongly affects electron transfer thermodynamics which, being reasonably located in the normal region of the Marcus parabola, becomes less exergonic and thus slower and less competitive towards intrinsic deactivation of the fullerene singlet state. This dendritic effect is in line with the molecular dynamics studies which suggest that the central OPV unit is more and more protected by the dendritic branches when the generation number is increased. Actually, the calculated structure of **23** shows that the two dendrons of third generation are able to fully cover the central OPV core (Fig. 12).

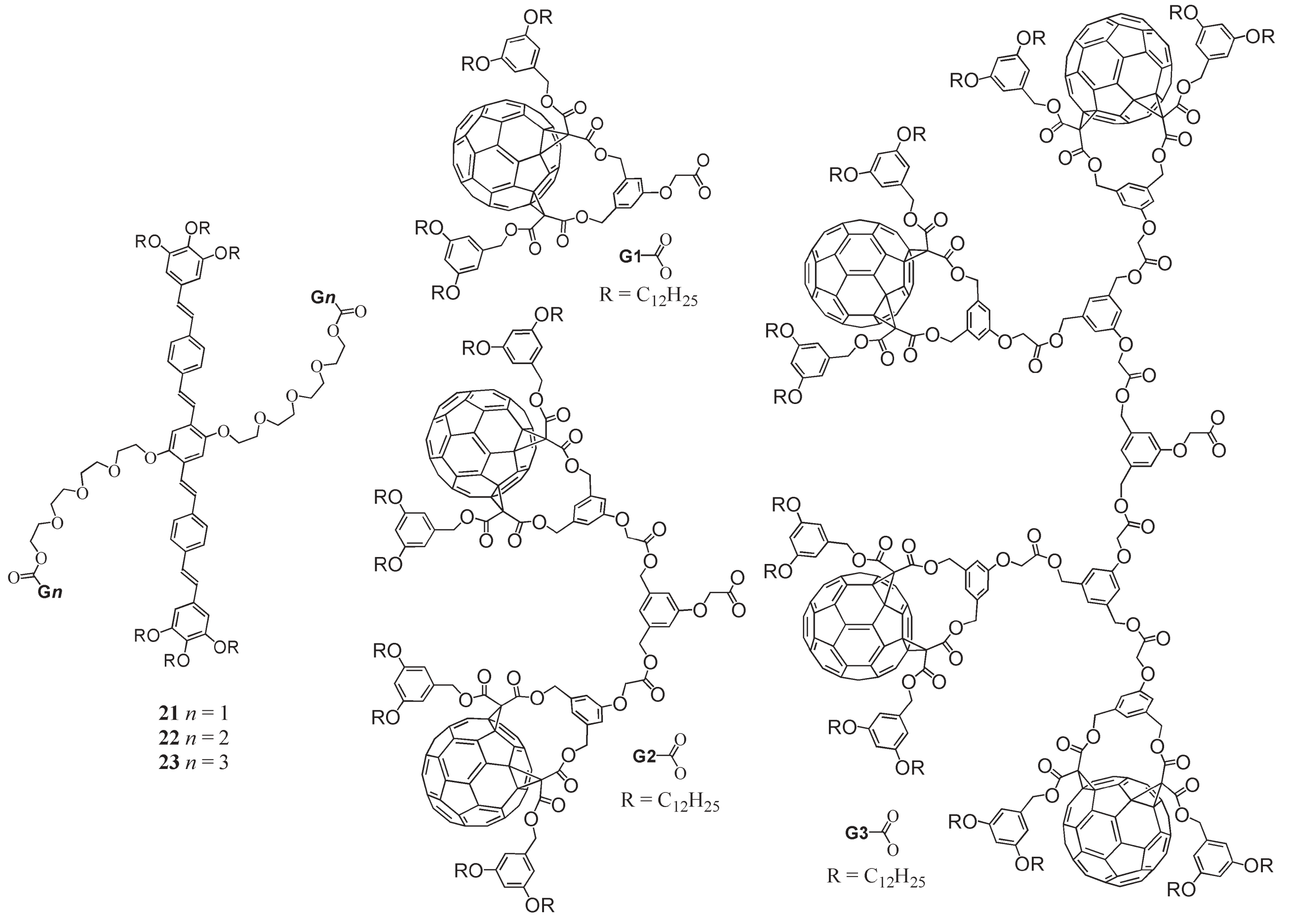


Fig. 11 Dendrimers with an OPV core and peripheral fullerene subunits.

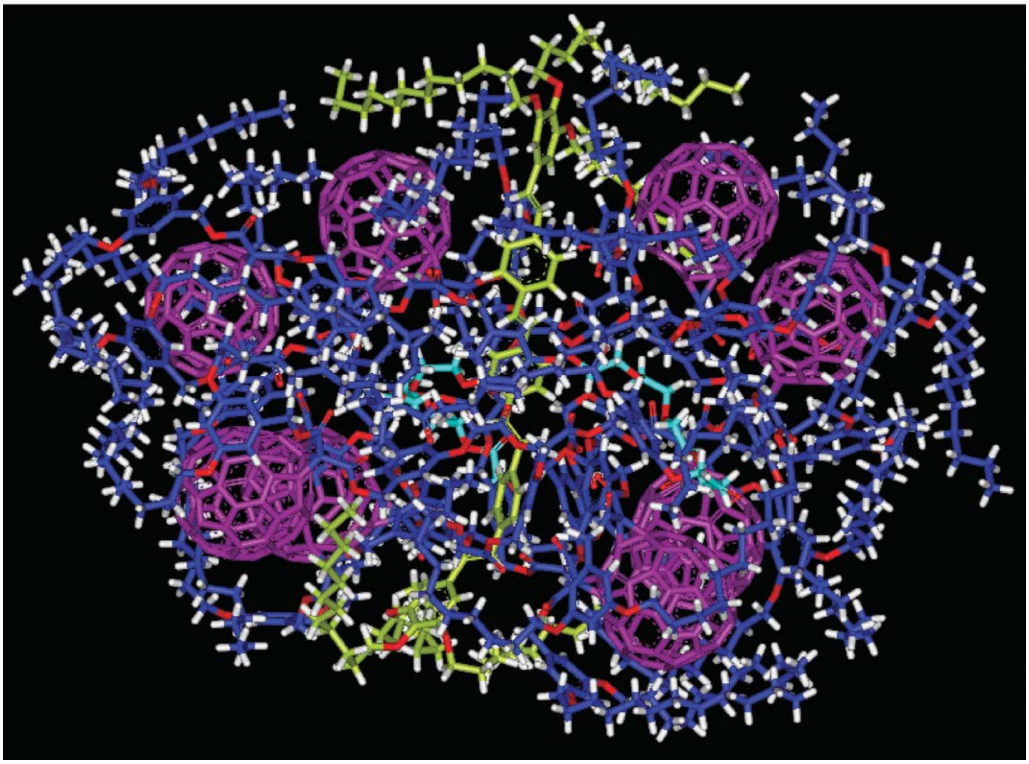
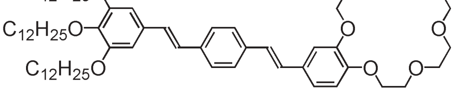


Fig. 12 Snapshot of the theoretical structure of fullerodendrimer **23** at 300 K obtained from a molecular dynamics calculation. The molecular dynamics studies have been performed on SGI Origin 200 and Octane^2 workstations using the Discover 3 software from Accelrys (www.accelrys.com) with the pcff forcefield. The previously minimized structures were allowed to equilibrate for 500 ps at a 300 K isotherm by the MD simulation (in the NVT ensemble with a time step of 1 fs).

Supramolecular fullerene–OPV conjugates

Whereas research focused on the use of C_{60} as the acceptor in covalently bound donor–acceptor pairs has received considerable attention, only a few related examples of fullerene-containing non-covalent systems have been described so far.[29,30] The assembly of the two molecular components by using supramolecular interactions rather than covalent chemistry appears, however, particularly attractive since the range of systems that can be investigated is not severely limited by the synthetic route. As part of this research, we have recently developed a non-covalent approach based on the self-assembly of C_{60} derivatives bearing an ammonium unit with crown ethers for the preparation of photoactive supramolecular systems.[31] For example, complexation of methanofullerene **24** with the OPV–crown ether conjugate **25** has been investigated (Fig. 13).[32] The K_a value for the 1 : 1 complex deduced from the complexation-induced changes in chemical shifts of the 4-(aminomethyl)benzyl protons in ^{1}H NMR binding titrations ($CDCl_3$, 298 K) was determined to be 3.5×10^3 M^{-1}.

The complexation between **24** and **25** was also investigated in CH_2Cl_2 by luminescence studies. Evidence for an intramolecular quenching of the OPV excited state by the fullerene moiety in [(**24**)·(**25**)] was obtained from the experiment depicted in Fig. 14. Addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) (1.5 equiv.) to the 1 : 1 mixture of **24** and **25** in CH_2Cl_2 causes an increase of the OPV emission. Actually, the fluorescence intensity of the resulting solution was found to be similar to that of a reference solution containing **25** and methanofullerene derivative unable to form a complex with **25**. In other words, the treatment with a base deprotonates the ammonium moiety of **24** and, thereby, disrupts the non-covalent bonding interactions that brought the components together. Addition of trifluoroacetic acid (2 equiv.) to the CH_2Cl_2 solution regenerates the ammonium center, thus allowing the formation of the supramolecular complex, and the luminescence intensity of final solution is the same as that of the starting 1 : 1 mixture of **24** and **25**. The observed decrease in luminescence intensity originates most probably from energy transfer from the photoexcited OPV to the C_{60} acceptor in the supramolecular complex [(**24**)·(**25**)]. Finally,



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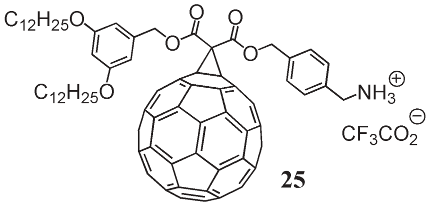

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Fig. 13 Compounds **24** and **25**.

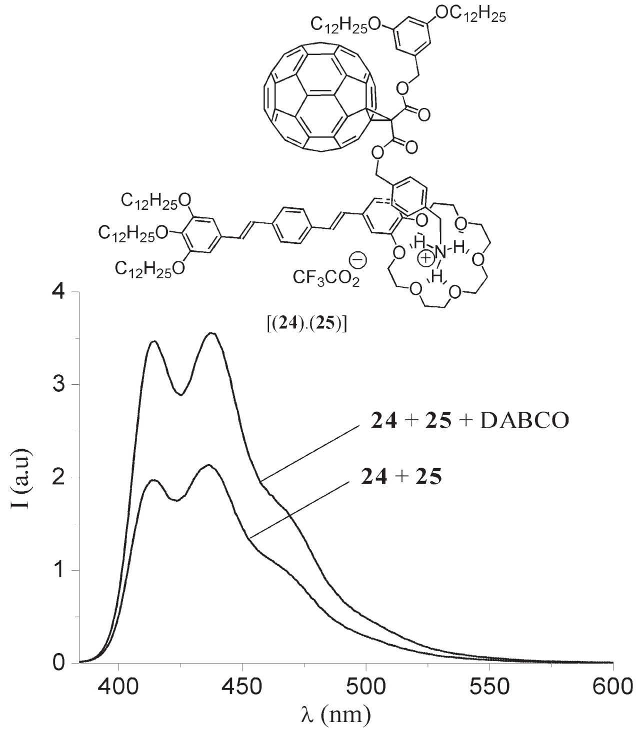


Fig. 14 Emission spectra (λ_{exc} = 372 nm corresponding to the maximum of absorption of **24**) of an equimolar mixture of **24** and **25** in CH_2Cl_2 before and after addition of DABCO (1.5 equiv.).

the association constant for the binding of **24** to **25** was also determined by a fluorescence titration in CH_2Cl_2. The corresponding K_a value was similar to the one deduced from the NMR binding studies.

The non-covalent OPV–fullerene system [(**24**)·(**25**)] is a photoactive supramolecular device. However, the ammonium–crown ether interaction is the only recognition element responsible for the association of the two components. As a result, the binding constant found for the complex obtained from **24** and **25** is rather low and only a small fraction of the two components are effectively associated in solution. This encouraged us to design a new fullerene–ammonium derivative capable of providing additional recognition elements in order to increase the association constants. The C_s symmetrical fullerene bis-adduct **26** (Fig. 15) was prepared.[33] When compared to compound **24**, additional phenyl units have been introduced to favor the occurrence of intramolecular π–π interactions in the supramolecular complex resulting from the binding of ammonium **26** to crown-ether **25**.

The complexation between **26** and **25** was investigated in CH_2Cl_2 by fluorescence binding studies. The K_a value thus determined (K_a = 6.3 × 10^4 M^{-1}) revealed a strong stabilization of the supramolecular complex. Effectively, the association constant between OPV **25** and fullerene **26** is increased by more than one order of magnitude when compared to the K_a value found for the complexation of **25** with cation **24**. The latter observation can be explained by a sum of secondary intramolecular weak interactions such as π–π stacking or hydrophobic associations in [(**25**)·(**26**)].

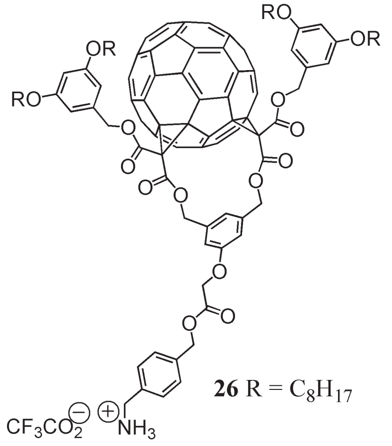


Fig. 15 Compound **26**.

The assembly of the C_{60}-ammonium cation **26** with OPV derivative **27** bearing two crown ether moieties (Fig. 16) was also investigated.[33] ES-MS studies revealed the formation of the supramolecular complex [$(\mathbf{26})_2$·(**27**)]. Effectively, the peak corresponding to this complex after loss of the counteranions was observed at *m*/*z* = 2417.8 (calculated *m*/*z*: 2417.9) in the mass spectrum obtained from a mixture of **27** (1 equiv.) and **26** (2 equiv.).

Here again, we took advantage of the efficient quenching of the OPV emission by the C_{60} moiety upon complexation of **27** with **26** to determine the K_a values by luminescence titrations. In this case, the processing of the titration data led to the determination of two binding constants defined by equilibria (1) and (2):

$$\mathbf{26}+\mathbf{27} \overset{K_1}{\rightleftarrows} [(\mathbf{26})\cdot(\mathbf{27})] \qquad K_1=\frac{[(\mathbf{26})\cdot(\mathbf{27})]}{[\mathbf{26}][\mathbf{27}]} \tag{1}$$

$$[(\mathbf{26})\cdot(\mathbf{27})]+\mathbf{26} \overset{K_2}{\rightleftarrows} [(\mathbf{26})_2\cdot(\mathbf{27})] \qquad K_2=\frac{[(\mathbf{26})_2\cdot(\mathbf{27})]}{[\mathbf{26}][(\mathbf{26})\cdot(\mathbf{27})]} \tag{2}$$

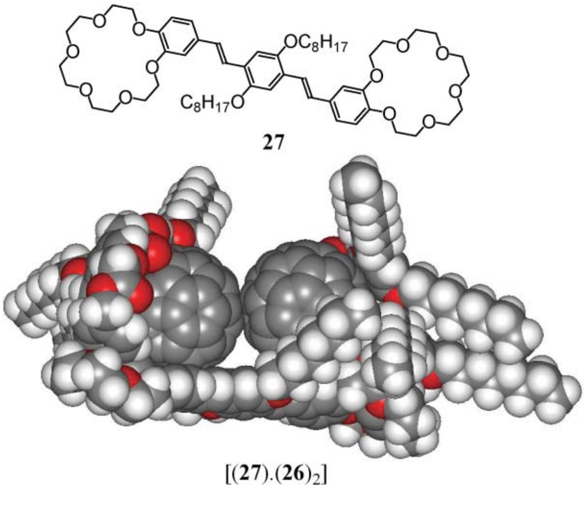


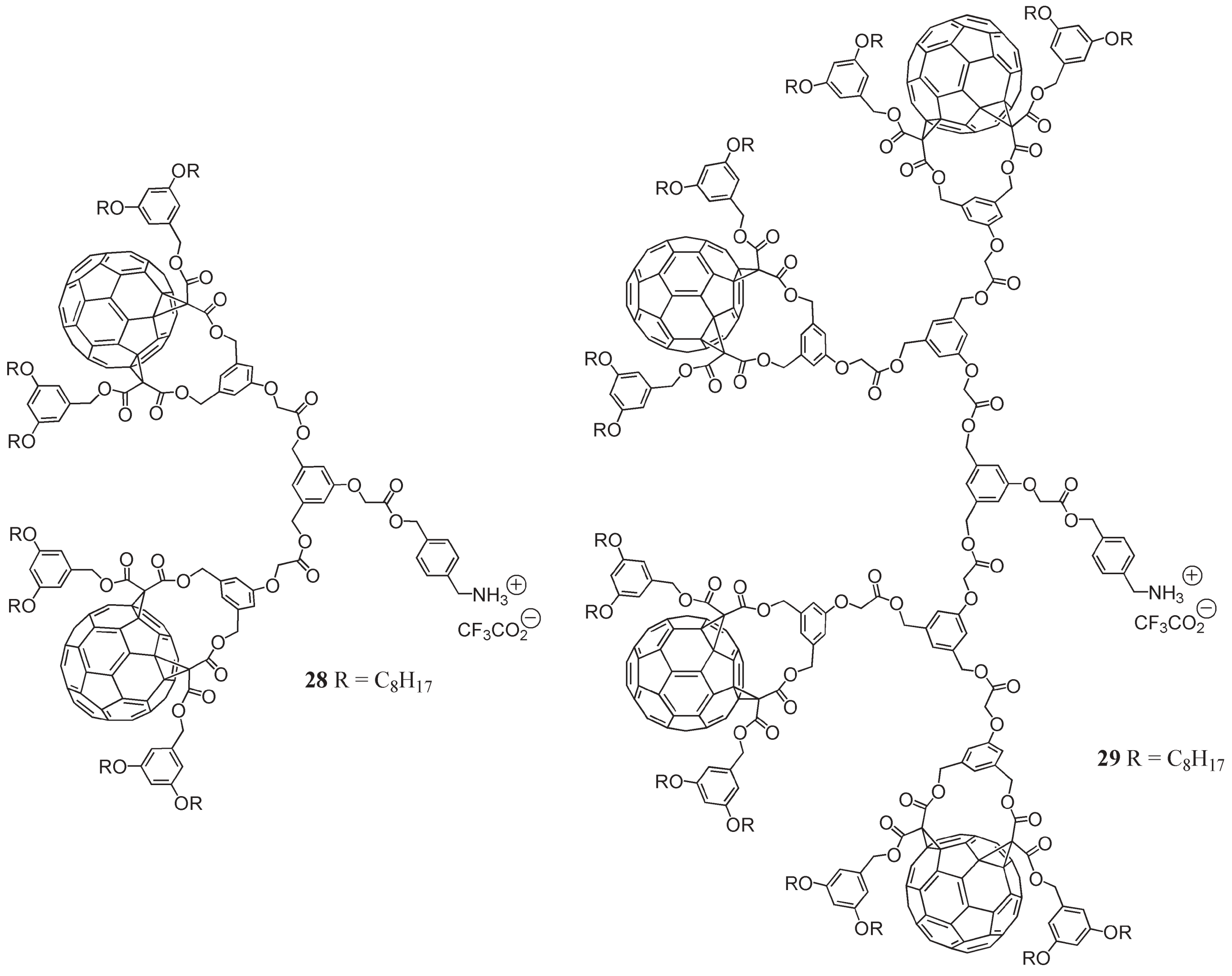
Fig. 16 Calculated structure of the supramolecular complex [$(\mathbf{26})_2$·(**27**)] (molecular modeling performed with *Spartan*).

Values of 10^4 and 3.98×10^4 M^{-1} were found for K_1 and K_2, respectively. Interestingly, the ratio $K_2/K_1 \approx 4$ is significantly larger than 0.25 which is the value expected for a statistical model of two identical binding sites.[34] The later observation clearly indicates that the stability of the supramolecular complex [(**26**)$_2$·(**27**)] is significantly higher than that of its analogue [(**26**)·(**27**)] due to positive interactions. Our thermodynamic data suggest a structure in which the two C_{60} units of [(**26**)$_2$·(**27**)] strongly interact through π–π stacking interactions as observed in the calculated structure of the 2 : 1 supramolecular complex depicted in Fig. 16.

The positive cooperative effect evidenced for the self-assembly of the 2 : 1 complex [(**26**)$_2$·(**27**)] prompted us to increase the number of C_{60} units attached on the ammonium building block in order to generate additional possible intramolecular interactions between the two guests in the 2 : 1 assembly (Fig. 17).[35]

For the 2 : 1 non covalent arrays obtained from **27** and **28**–**29**, the K_2/K_1 ratio (9 for **28** and 16 for **29**) are significantly larger than 0.25 which is the value expected for a statistical model and clearly indicates positive intramolecular interactions in the 2 : 1 associates. The latest observation may be ascribed to strong intramolecular fullerene-fullerene interactions between the two dendritic guests within the 2 : 1 supramolecular assembly. This hypothesis is also supported by the absence of any positive interactions for the 2 : 1 complex obtained from **27** and an ammonium derivative lacking the fullerene subunits. Finally, it is also important to highlight that the K_2/K_1 ratio is significantly increased when the size of the dendritic branches is increased. In other words, the cooperative effect is more and more effective when the number of C_{60} units is increased. This positive dendritic effect further confirms that intramolecular fullerene-fullerene interactions must be at the origin of the observed cooperative effect. These results show that the size of dendritic building blocks does not constitute a severe limitation for the self-assembly of large dendritic architectures. Furthermore, it appears that the stability of the highest generation supramolecular ensemble is increased due to the increased number of possible secondary interactions within the self-assembled structure.

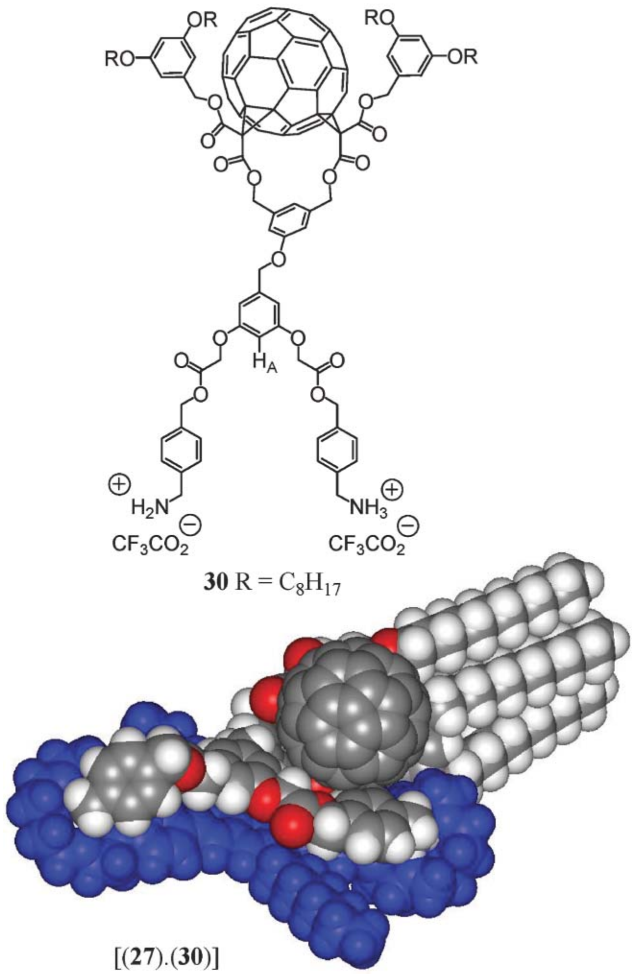
Finally, the bis-ammonium fullerene ligand **30** (Fig. 18) was designed to form a 1 : 1 macrocyclic supramolecular complex with the bis-crown ether receptor **27**.[36] Owing to the good complementarity of the two components, the bis-cationic substrate **30** can be *clicked* on the ditopic crown ether derivative **27** (Fig. 18).



28 R = C_8H_{17}

29 R = C_8H_{17}

Fig. 17 Fullerodendrimers **28** and **29**.



30 R = C_8H_{17}

[(**27**).(**30**)]

Fig. 18 Compound **30** and calculated structure of the supramolecular complex [(**27**)·(**30**)] (molecular modeling performed with *Spartan*).

The binding behaviour of bis-ammonium **30** to the bis-crown ether receptor **27** was first investigated by ^{1}H NMR in $CDCl_3$ at 298 K. The comparison between the ^{1}H NMR spectra of **27**, **30** and an equimolar mixture of both components revealed complexation-induced changes in chemical shifts. In particular, a dramatic down-field shift is seen for the signal of H_A (see Fig. 18) in **30** upon addition of **27**. The latter observation is in good agreement with the formation of a macrocyclic 1 : 1 supramolecular complex in which proton H_A is located on top of the π-conjugated system of **27** (Fig. 18). The formation of a 1 : 1 complex was further evidenced by ESMS. The positive ES mass spectrum recorded under mild conditions from a 1 : 1 mixture of **27** and **30** is dominated by a doubly charged ion peak at m/z = 1723.1 which can be assigned to the 1 : 1 complex without the trifluoroacetate counteranions (calculated m/z = 1723.11). As already seen for the previous examples, the strong emission of **27** is quenched upon binding of **30** by an efficient intramolecular process in complex [(**27**)·(**30**)], thus allowing to easily determine the binding constant by luminescence titrations. The stability constant of [(**27**)·(**30**)] was found to be 2.51×10^6 M^{-1}. The comparison with the thermodynamic data of crown-ethers with simple ammonium guests shows a coordination stronger by two to three orders of magnitude. This is mainly associated to the two-center host–guest topography. Similarly to the "click chemistry" concept of Sharpless,[37] the "supramolecular click chemistry" principle described for the binding of **30** to **27** is a powerful and selective process for the preparation of stable macrocyclic non-covalent arrays. This approach is modular and appears easily applicable to a wide range of functional groups for the preparation of new supramolecular architectures with tunable structural and electronic properties.[38]

Conclusions and outlook

Following the preparation of the first photovoltaic devices from C_{60}–OPV conjugate **1**, a great deal of attention has been devoted to C_{60} arrays substituted with various π-conjugated oligomers such as oligophenyleneethynylene, oligothiophenes, and related systems.[39] The photophysical properties of these C_{60}–(π-conjugated oligomer) dyads have been extensively studied and found similar to the one described herein for the C_{60}–OPV systems. A characteristic feature in all these dyads is an ultrafast energy transfer from the lowest singlet excited state of the conjugated system to populate the fullerene singlet. This first event can be followed by an electron transfer depending on the donating ability of the oligomer, on structural factors and on the solvent polarity. The peculiar electronic properties of C_{60}–OPV conjugates led also to the development of dendritic systems with interesting light harvesting properties or for evidencing original dendritic effects. Finally, several stable supramolecular arrays assembling conjugated oligomers and fullerenes have been reported.

Among their potential use as active materials in photovoltaic devices, C_{60}–(π-conjugated oligomer) hybrid systems offer also interesting perspectives for optical limiting or photodynamic therapy applications. Finally, the wire-like behaviour of the OPV units linking the C_{60} acceptor to various donors opens the way to use related compounds as integrated components in the construction of optoelectronic devices and nanotechnology.

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